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Small carborane ligands as spectators and as players

Russell N. Grimes *

Department of Chemistry, University of Virginia, Charlottesville, VA 22901, USA

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Abstract

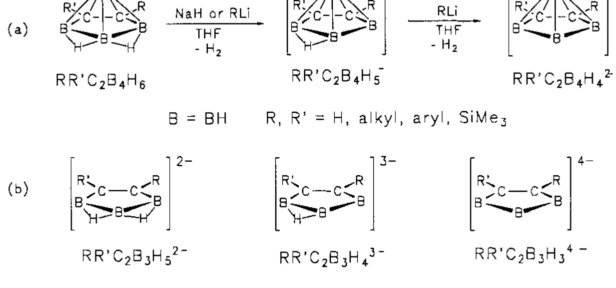
A quarter-century of development of the chemistry of small metallacarboranes—metal sandwich complexes of ligands incorporating planar C_2B_3 or pyramidal C_2B_4 clusters—has seen many surprises, including the synthesis and isolation of the first thermally and oxidatively stable triple-decker (and larger) sandwiches, the discovery of metal-promoted oxidative fusion of carborane ligands, and a broad and rich array of structurally novel cluster and sandwich compounds that involve most of the transition elements and main group metals. In many of these species the metal-bound carborane unit formally replaces Cp or Cp*, and functions as a 'spectator' ligand, influencing the reactions of the metal center through electronic interaction. In other situations, some of which have been revealed only recently, the carborane ligand is directly involved in reactions with attacking substrates and undergoes permanent change in structure and/or composition. In this mode, the carborane as a ligand displays very different chemical behavior from that of its aromatic hydrocarbon counterparts and can lead to reactions and products that have no analogies in metallocene-based chemistry. Both roles are not only of interest from a pure chemistry viewpoint, but also have potential application as tools in directed synthesis. The chemistry described in this short review represents but one aspect of the development of organometallic-boron cluster chemistry in many laboratories, an area whose significance is growing as the new millennium approaches. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metallacarboranes; Sandwich compounds; 'Spectator' ligand

1. Introduction

Metal sandwich complexes of the pentagonal–pyramidal $RR'C_2B_4H_{6-n}^{n-}$ ($n = 1, 2$) and planar $RR'C_2B_3H_{7-n}^{n-}$ ligands ($n = 2, 3, 4$) (Scheme 1) have a rich and diverse chemistry that in many respects exceeds that of the metallocenes [1]. Neutral *nido*-$RR'C_2B_4H_6$ carboranes, which can be prepared on a 100-gram scale from B_5H_9, RC≡CR′ alkynes, and triethylamine in diethyl ether at 0°C [2], contain two acidic B–H–B hydrogens. One or both of these protons can be removed by organolithium reagents to generate the corresponding $RR'C_2B_4H_5^-$ or $RR'C_2B_4H_4^{2-}$ anions (Scheme 1(a)). The pyramidal C_2B_4 anions (Scheme 1(a)) exist both as free ions in solution and as metal sandwich complexes, but the planar C_2B_3 ligands are known only in complexed form.

Since η^5-bound metal complexes of the C_2B_3 and C_2B_4 ligands are equally well described as heteroatom-containing boron clusters and as organometallic sandwich compounds, they occupy a strategic location at the intersection of two major areas of contemporary inorganic chemistry. The η^5-coordination of metal centers to planar C_2B_3 faces in these species is analogous to metallocene bonding in both an electronic and a steric sense, making them useful as building blocks for the construction of multicluster or multidecker sandwich structures [1d,f].



Scheme 1.

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* Tel.: + 1-804-924-3150; fax: + 1-804-924-3710.
E-mail address: rng@virginia.edu (R.N. Grimes)

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2. The metallocene analogy

As ligands, these carborane ions are formal 6-electron π-donors to transition metal centers via metallocene-like interactions between molecular orbitals on the basal C_2B_3 ring and suitable metal orbitals; like the icosahedral-fragment $C_2B_9H_{11}^{2-}$ (dicarbollide) ions [3], they are counterparts of $C_5H_5^-$ (Cp^-) and $C_5Me_5^-$ (Cp^{*-}) as well as benzene and other arenes. The carborane-to-metal electron transfer is clear from quantitative evidence including electrochemical [4], structural [1], NMR [1], and other data—for example, in the observation of higher reduction potentials of the metal centers in neutral $CpM^{III}(RR'C_2B_4H_4)$ complexes compared to those of isoelectronic $[Cp_2M^{III}]^+$ species [4a]—and in the ability of the carborane anions to form air-stable, thermally robust sandwich complexes with high-oxidation state metal centers such as Co^{IV} and Ni^{IV}. (Incidentally, the fact that these carborane ligands are electron-rich donors underlines the irrelevance of labeling such nonclassical boron clusters as 'electron-deficient'.) Although the heterocyclic carborane anions are of lower symmetry than Cp^-, they nonetheless usually bind strongly to transition metals in pentahapto (η^5) fashion, such that the metal–carbon and metal–boron links are about equal in length and strength. The $RR'C_2B_4H_5^-$ and $RR'C_2B_4H_4^{2-}$ ions both complex in this way; when the monoanion is employed, its B–H–B proton is often retained in the metallacarborane product as a metal-bound (M–H), bridging (M–H–B), or face-bound ($M-H-B_2$) hydrogen [1d].

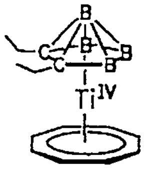
Bis(carboranyl) complexes such as $H_2Fe^{II}(Me_2C_2B_4H_4)_2$ or mixed-ligand species such as $CpCo^{III}(Me_2C_2B_4H_4)$ are direct analogues of metallocenes, but there are significant differences. Owing to the lower electronegativity of boron vs. carbon, the metal binding to the carborane ring is more covalent in character than that in metal–hydrocarbon bonds, and most metal complexes of the carborane ligands are exceptionally stable to air-oxidation and to thermal degradation (this is also generally true of the icosahedral and other metallacarborane structural types [1a,b,3]). Another prominent characteristic of the small carborane ligands is their ability to function in two distinctly different modes. As relatively passive 'spectators' in some complexes, they exert electronic (and in some cases steric) influence on the reactivity at the metal center, but do not interact directly with incoming substrate species. In other situations, the carborane units are actively involved as participants in the reaction, and experience net change in their structure and/or cage substitution. The versatile reactivity of the carborane ligands not only leads to a very rich and often novel chemistry, but also allows the facile introduction of substituents and functional groups, making it feasible to tailor the ligands *while they are bound to the metal*—a task that can be problematic in metallocene chemistry [5].

The dual role of the small carborane ligands as spectators and as active participants is the central theme of this article. General reviews of the metallacarborane field are available elsewhere [1]; here I present a selection of examples that illustrate the influence of small carborane ligands, directly and indirectly, on the structure and properties of metal sandwich complexes. Most chemistry of these ligands falls clearly into either the 'player' or 'spectator' category—the carborane moiety either undergoes net change or it does not—but in some instances both roles are evident in the same reaction system, as will be seen.

3. Early transition metal complexes

3.1. Stabilization of unusual organometallics

In many cases the influence of small carborane ligands is directed through the metal center to other (non-carborane) ligands bound to the metal. For example, the cyclooctatetraenyl species **1** and **2**, whose structures have been established by X-ray crystallography [6], are rare examples of air-stable first-row transition metal sandwich complexes of planar η^8-$C_8H_8^{2-}$. As these compounds contain formal Ti^{IV} and V^{IV}, respectively, their stability is a notable demonstration of the effects of carborane–metal complexation. The V^{4+} ion in **2** is evidently the smallest metal center that has been shown to bind equally to all of the carbon atoms in a planar C_8 ring, and the unreactivity of this compound toward O_2 is remarkable for a paramagnetic 17-electron species.



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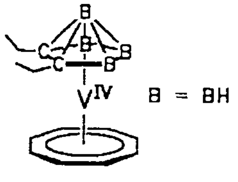
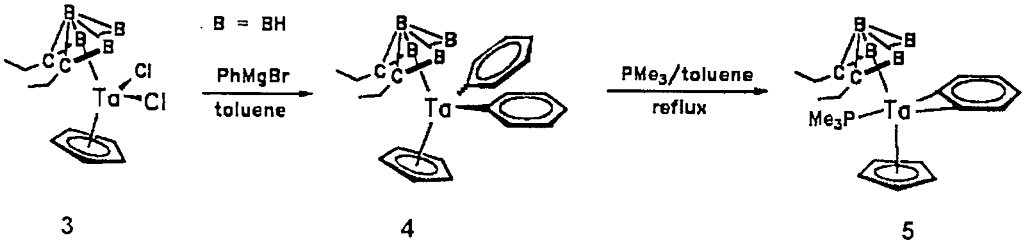
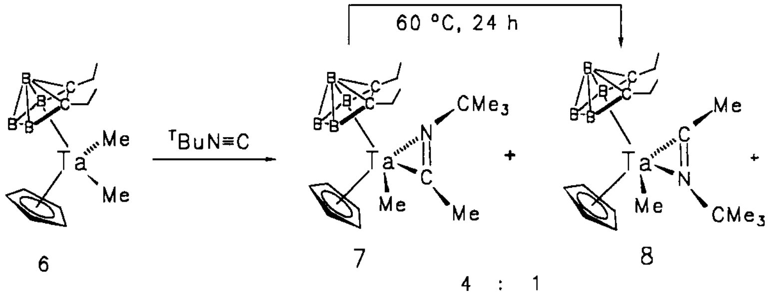


2

The stabilizing capability of the carborane ligands is revealed again in the air-stable benzyne complex **5**—a very rare genre—that was prepared as shown in Scheme 2 [7]. It should be noted that the formal oxidation state of tantalum in compounds **3**–**5** is +5, and that the $(Et_2C_2B_4H_4)Ta^VCp^{2+}$ moiety is electronically analogous to the titanocene dication $Ti^{IV}Cp_2^{2+}$. Compound **5** is unreactive with a variety of substrates including MeOH, acetone, MeCN, or alkynes, and its phosphine group is non-labile [7]. In the absence of



Scheme 2.



Scheme 3.

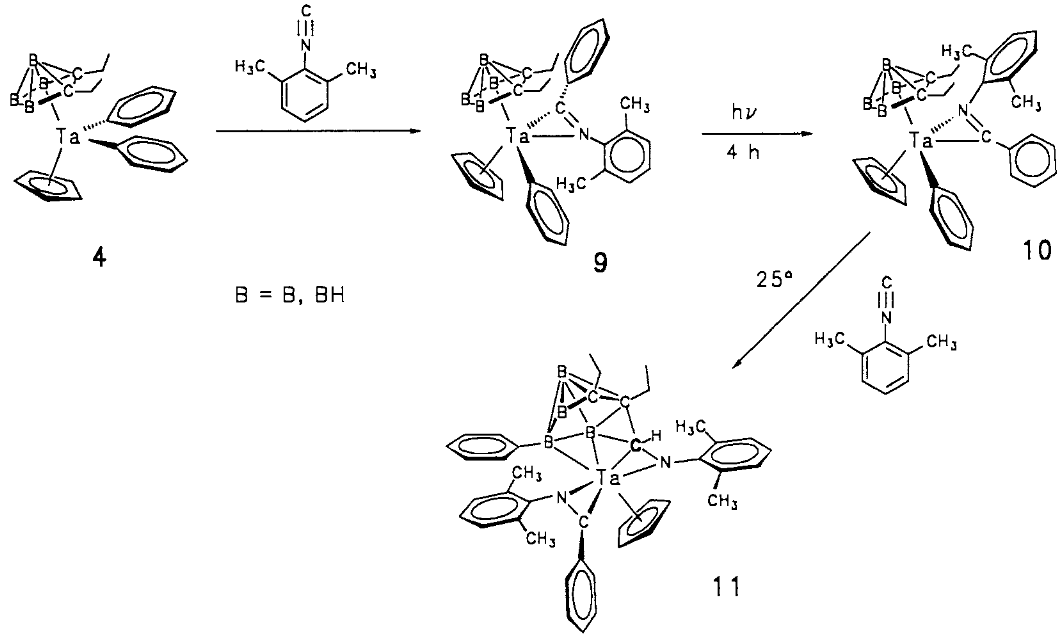
phosphines, however, Ta–benzyne complexes are quite reactive, as will be seen.

3.2. Insertion of unsaturated organic substrates

Further examples of the influence of the carborane ligand on tantalum chemistry are found in the behavior of **4** and its dimethyl counterpart **6** toward nitriles, isonitriles, alkenes, and alkynes [8,9]. Unlike isoelectronic Cp–Group IV complexes [10], **6** is unreactive toward these substrates under moderate heating, and requires UV irradiation [8,9]. Scheme 3 depicts insertions of *tert*-butyl isonitrile into Ta–CH_3 bonds in **6** to give isomeric products **7** and **8**, both of which were structurally characterized; the kinetically favored isomer **7** has an unfavorable steric interaction between the *tert*-butyl group and the carborane ligand, and rearranges completely to **8** on mild heating [7]. While nitrile insertions into metal–alkyl bonds are well known, the isolation and interconversion of η^2-iminoacyl isomers as in **7** and **8**, is rare. Again, the stabilization of these products can be understood as an effect of the transfer of electron density from the carborane ligand to the metal center.

The behavior of the diphenyl compound **4** toward bulky isonitriles has generated some novel chemistry. As illustrated in Scheme 4, one equivalent of 2,6-dimethylphenylisocyanide (DMPI) inserts into a Ta–Ph bond to form a single isomer, **9** (characterized by crystallography), which does not rearrange on heating but does isomerize to **10** under UV light [8]. These two isomers differ enormously in their reactivity toward isocyanides: while **9** is virtually inert toward DMPI, diphenylacetylene, or 2-butyne at 85°, **10** reacts instantly with DMPI at room temperature (r.t.) to generate the unique product **11.** An X-ray structural study of **11** has established that the isonitrile carbon atom (shown in boldface) has been incorporated into the cage framework, and the unsubstituted phenyl group on that carbon has migrated to the B(5) position on the carborane ring, the carbon atom acquiring a hydrogen in its place! Similarly, a product structurally analogous to **11** is apparently formed in the reaction of **10** with methyl isocyanide [8]. These cage insertions are notable both in terms of the novel metallatricarbaazaborane products formed and in the facility with which they occur.

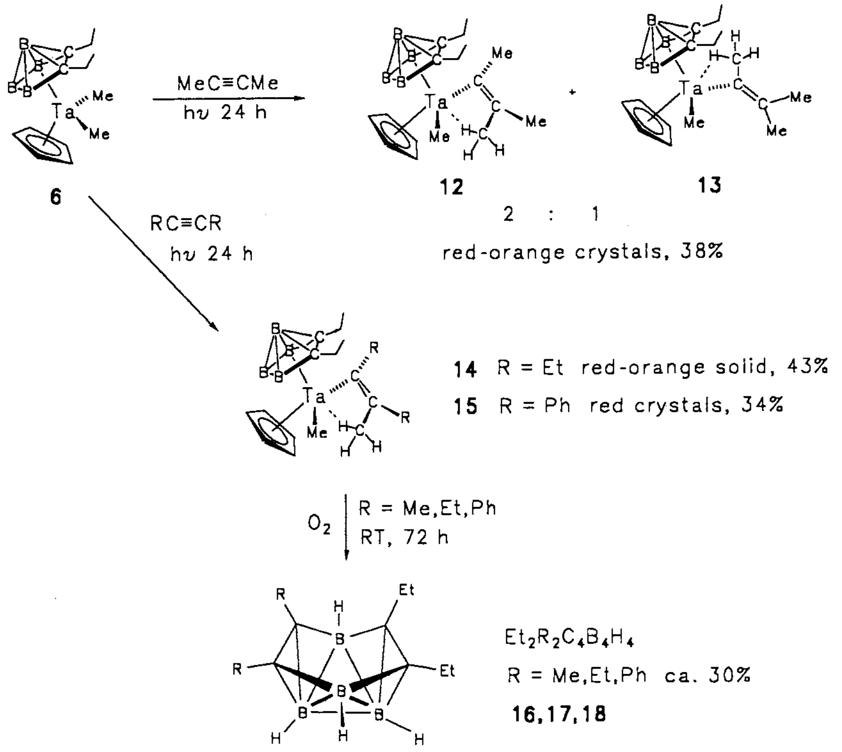
Unusual chemistry has also been encountered in the insertions of alkynes. As shown in Scheme 5, reactions of the dimethyltantalum complex **6** require photochemical activation [9], unlike the thermal reactions of isoelectronic Group IV metallocenes that typically generate methylidenes [10–13]. For example, **6** is thermally stable but reacts with alkynes under UV irradiation to give not methylidenes but vinyltantalum products. Thus, 2-butyne generates products **12** and **13**, whose noteworthy features are γ-agostic Ta–H_3C interactions (indicated from NMR evidence) that are sufficiently strong to stabilize the two regioisomers shown. Bulkier alkynes, in contrast, give only single isomeric products (**14**, **15**). In all of these complexes **12**–**15**, the carborane ligands are in ‘spectator’ mode and apparently unchanged, but on exposure to air at r.t. they interact in a remarkable way with the vinyl groups to generate



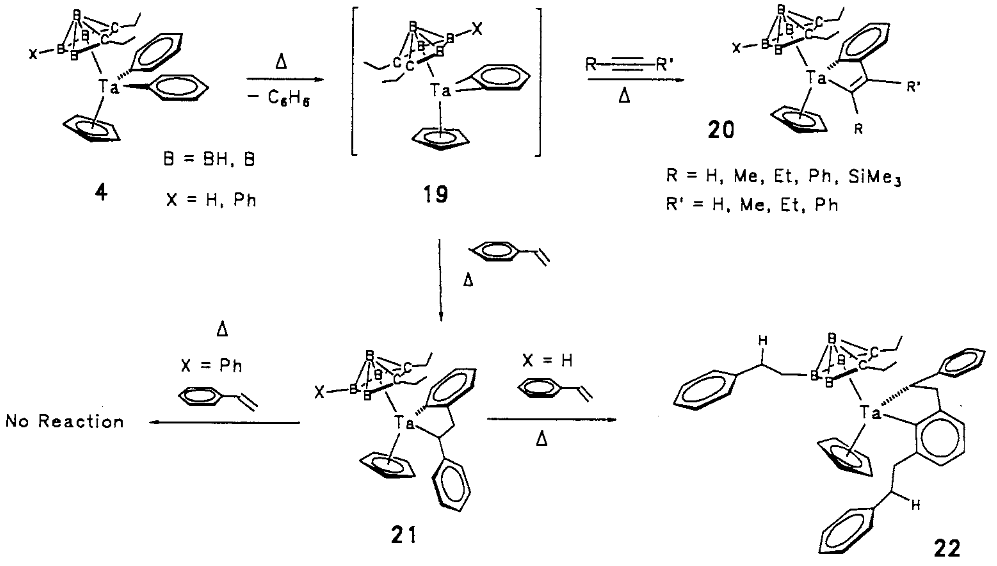
Scheme 4.

8-vertex $Et_2R_2C_4B_4H_4$ *nido*-carborane clusters **16**–**18** as shown at the bottom of Scheme 5 [9].

The C_4B_4 cage structure depicted for **16**–**18** is consistent with NMR data and is supported by a very recent X-ray structure determination of a closely related derivative, $H_4C_4B_4Et_4$, by Wrackmeyer and co-workers [14]. C_4B_4 carboranes have been reported previously [15–18]; for example, the diethyl–dimethyl derivative **16** was prepared in Sneddon's group by other routes, i.e. from $NiCl_2$ and $(Et_2C_2B_4H_4)Li_2$ with terminal alk-



Scheme 5.



Scheme 6.

ynes [15], and from $Et_2C_2B_4H_6$ and 2-butyne in the presence of a ruthenium phosphine catalyst [16]. In our work [9], the vinyl insertion into the C_2B_4 carborane cage is notable in that the C–Me bond, which was formed in the insertion of the alkyne into **6** as described above, is broken in the process despite the mild conditions. Thus, in the formation of clusters **16**–**18** the carborane ligand functions as an active player in a metal-promoted hydrocarbon insertion that has no parallel in metallocene chemistry.

In contrast to the dimethyltantalum complex **6**, which is thermally inert as discussed above, the diphenyl compound **4** behaves quite differently, reacting with alkynes under mild heating to generate metallaindenes **20**; these reactions evidently proceed via loss of benzene to form benzyne intermediates **19** which trap the alkynes, as illustrated in Scheme 6 [9]. In reaction with excess styrene, the unsubstituted carborane ligand (X = H) becomes actively involved, taking the remarkable course depicted leading to the B(5)-phenethyl-substituted product **22** whose structure has been established via X-ray crystallography. From detailed NMR studies, this sequence has been proposed to involve an agostic B–H···Ta interaction with the central BH unit. As shown, replacement of this hydrogen in **21** by phenyl blocks the reaction [9].

The ability of the C_2B_4 ligands to influence early transition metal chemistry has potential application in catalysis, an area that is currently under investigation in our laboratory [19]. Titanium complexes of the type $L_2Cl_2Ti(Et_2C_2B_4H_4)$ ($L_2 = 2PR_3$ or $R_2P(CH_2)_n$-PR_2) in combination with methylaluminum oxane catalyze the polymerization of ethylene and propylene at r.t. and atmospheric pressure. While many Ziegler–Natta catalysts are currently available, three potential advantages of the Ti–carborane species can be cited: (1) they are readily tailored via substitution on the metal and/or the carborane ligand, (2) they are more stable than most Z–N catalysts, and (3) they are remarkable in exhibiting catalytic activity while apparently retaining non-labile phosphino groups on the metal. These properties suggest a possible future commercial role for suitably tailored small metallacarborane-based polymerization catalysts.

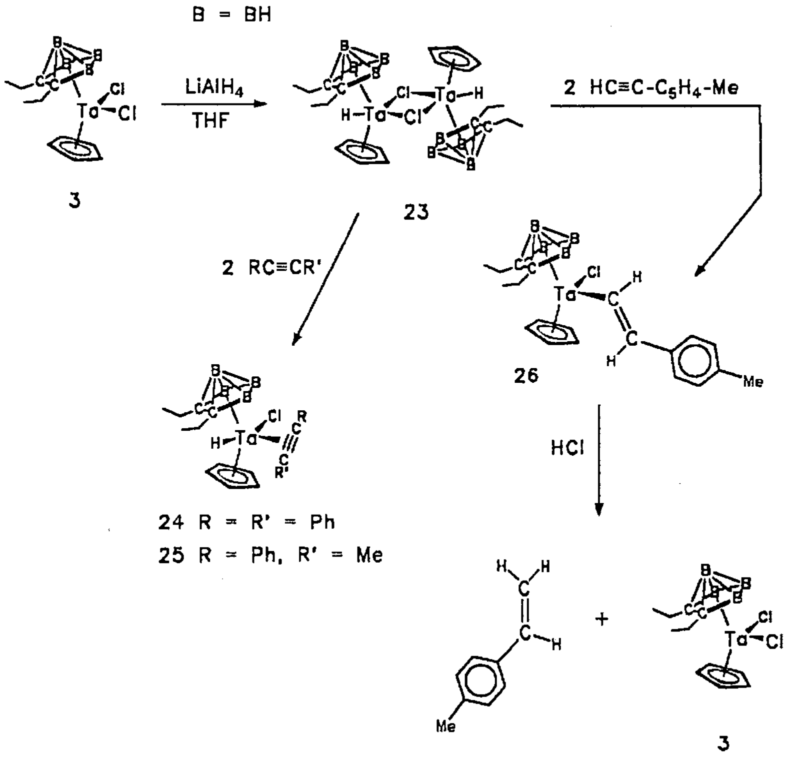
As another example of C_2B_4 ligands as spectators in early transition metal complexes, the hydridotantalum dimer **23**, shown in Scheme 7, is a Ta^V analogue of Schwartz's reagent [$Cp_2Zr(H)Cl$], well known for its ability to form alkyl or alkenylzirconium complexes via insertion of alkenes and alkynes into the Zr–H bond [20]. In contrast to Schwartz's reagent, **23** is soluble in benzene and THF at r.t. and reacts with PhC≡CPh or PhC≡CMe to generate the hydrido–alkyne products **24** and **25**, the first known examples of d^0–alkyne complexes [21] (Scheme 7). On treatment of **23** with *p*-toluyl acetylene, however, the *trans* complex **26** was formed exclusively, demonstrating *cis*-addition to the Ta–H bond. Treatment of the latter product with an equivalent of anhydrous HCl liberated *p*-methyl styrene and the dichlorotantalum complex **3** [21]. Although studies in this area are still in an early, exploratory stage, these findings furnish further evidence that formal replacement of Cp–metal units with isoelectronic C_2B_4–metal groups can materially alter the reactivity toward organic substrates. It seems not unreasonable to expect that such complexes may find useful roles in organic synthesis.

4. Late transition metal complexes

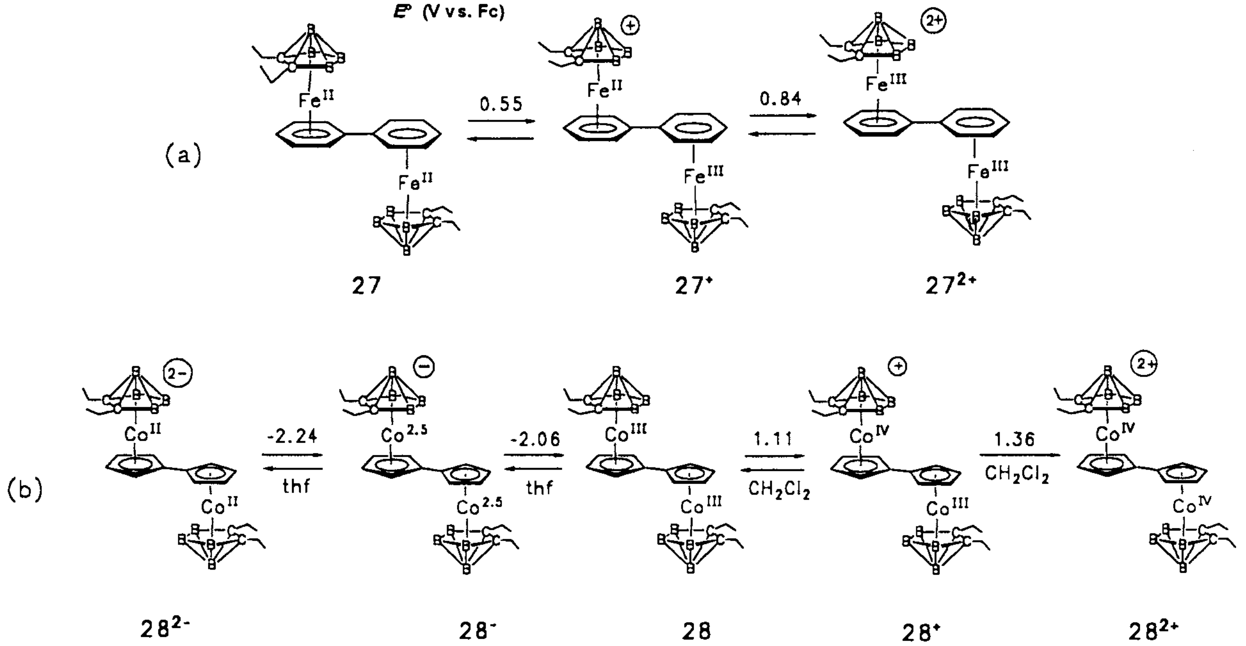
4.1. Bimetallic systems

A striking property of the small carborane ligands is their ability to stabilize both high and low formal metal oxidation states, illustrated by the bimetallic neutral complexes **27** and **28** in Scheme 8 [4b,f].

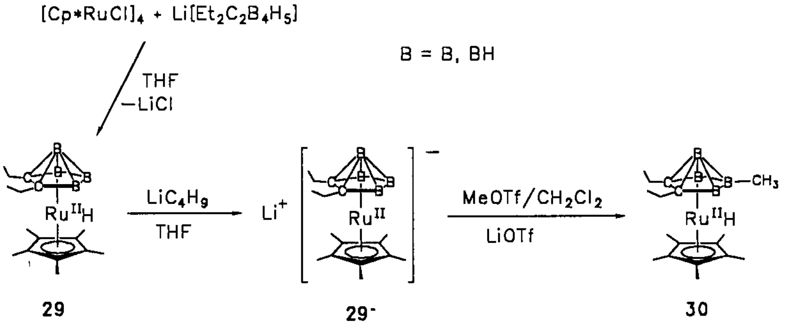
The air-stable diiron complex **27** is readily oxidized to the mixed-valent d^5–d^6 species $\mathbf{27}^+$, a trapped-valence system, and the d^5–d^5 dication $\mathbf{27}^{2+}$; the arene–Fe^{III} sandwich binding featured in these complexes is



Scheme 7.



Scheme 8.



Scheme 9.

very rare in organometallic chemistry generally. The fulvalene-bridged species **28**, a red air-stable compound, is a d^6–d^6 system that exhibits behavior unknown in any bimetallic metallocene complex: it undergoes reversible reduction to mono- and dianions (**28**$^-$ and **28**$^{2-}$), reversible oxidation to a d^6–d^5 monocation (**28**$^+$), and a further irreversible oxidation to a d^5–d^5 dication (**28**$^{2+}$). The mixed-valent complex **28**$^-$, an analogue of the bicobaltocene cation, is a fully delocalized (Class III) mixed-valent species as shown from electrochemical, ESR, optical spectra, and IR spectra [4b,f]. The IR B–H stretching bands in these and other small-carborane metal sandwich complexes are powerful diagnostic indicators of electron delocalization, owing to their extraordinary sensitivity to the oxidation state of the bound metal center (ca. 40 cm^{-1} per electron equivalent). Further discussion of these findings appears elsewhere [4f].

4.2. Hydridometal complexes

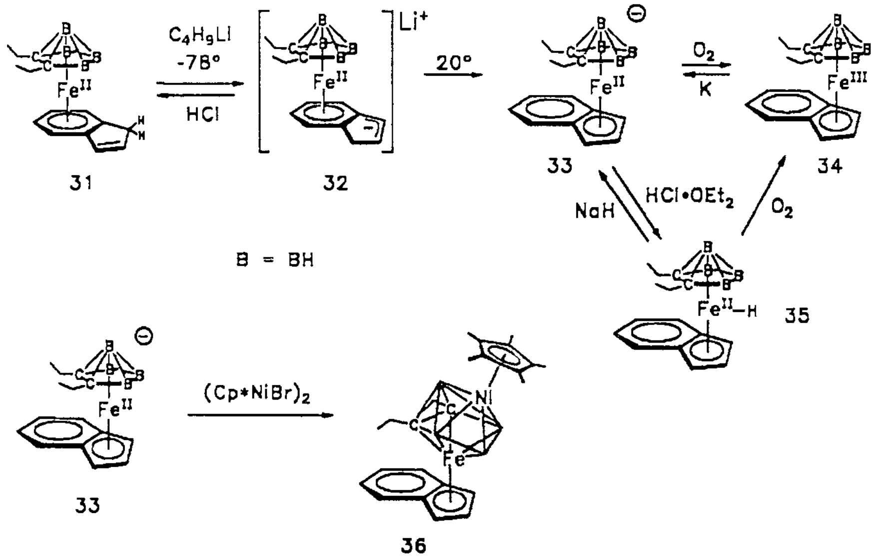
The $RR'C_2B_4H_4^{2-}$ ligands, by virtue of their donation of electron density to metal centers, also stabilize the binding of H^+ ligands to the metal, especially in complexes of Co, Fe, and Ru. Although the metal-bound protons are usually readily removed by nucleophiles such as alkyllithium reagents, complexes containing $M–H^+$ and even $M(H^+)_2$ can often be isolated as air-stable compounds [1,22]. A recent example involving ruthenium, depicted in Scheme 9, illustrates the synthesis of the metal hydride **29**, which was characterized by spectroscopic methods and X-ray crystallography [23], as well as its deprotonation and methylation of the anion to give the B-methyl product **30**. The latter process is highly unusual, involving a rearrangement of the $Ru–CH_3$ complex that presumably forms initially, very likely via an agostic B···H···M interaction. Clearly, in this case as in several others described in this article, the carborane ligand crosses the line from a spectator role to that of an active participant, undergoing permanent change.

The chemistry of metallacarborane double-decker to hexadecker sandwich complexes is replete with examples of $Co–H^+$ and $Fe–H^+$ bonding, in modes that vary from pure M–H interactions (no other atoms involved) to M–H–M and M–H–B bridging and $M–H–B_2$ binding in which the proton caps a triangular M–B–B face [1a,b,d,24]. As already noted, the prevalence of these situations can be ascribed to the relatively high electron density that the carborane ligand produces in the region of the metal centers, making them much more attractive locations for protons than is typically the case in metallocenes.

Protons bound to metals also play a role in the oxidative fusion of small boron cluster anions in which, for example, a pair of $R_2C_2B_4H_4^{2-}$ ligands in complexes of the type $MH_x(R_2C_2B_4H_4)_2$ ($M = Co^{III}$, $x = 1$; $M = Fe^{II}$, $x = 2$) are converted under mild conditions to neutral $R_4C_4B_8H_8$ carboranes [1a,b,d,25]. This type of reaction has been found to occur in metallaborane as well as metallacarborane systems, and has been reviewed in detail recently [25].

4.3. Indenyliron complexes

The consequences of incorporating C_2B_4 ligands are also evident in other metal-hydrocarbon systems. The indenylferracarborane **31** (Scheme 10), when deprotonated and warmed to r.t., undergoes a haptotropic shift from the C_6 to the C_5 ring in **33**, and the anion **33** can be reversibly oxidized to the Fe^{III} species **34** as well as protonated to give neutral **35** [26]. In these transformations the carborane ligand is a spectator. However, treatment of the anion **33** with the $(Cp^*NiBr)_2$ dimer results in cage expansion via incorporation of nickel to generate the 8-vertex $FeNiC_2B_4$ polyhedral cluster **36** [26]. The dual role of the C_2B_4 ligand is thus clearly displayed in the indenyl–ferracarborane system which, depending on the attacking reagent, manifests behavior typical of both organometallic and boron cluster chemistry. Again, these unusual reactivity patterns can be qualitatively understood in terms of the strong covalent carborane–metal interaction that shifts electron density to the metal and effectively lowers the true charge (as distinct from the formal oxidation state) on the metal center.



Scheme 10.

4.4. Activation of C_5Me_5 ligands

An unexpected finding in recent work [27] was the coupling of cobaltacarboranes **37a–d** via linkage of the C_5Me_5 (Cp*) hydrogens on attack by *n*-butyllithium, as shown in Scheme 11. The orange, air-stable products **38a–d** were isolated in 28–56% yield.

Activation of Cp* is extremely rare [28] despite widespread use of this hydrocarbon ligand in organometallic research. A notable aspect of the reaction in Scheme 11 is that it evidently proceeds regardless of the nature of the substituent X on the carborane cage.

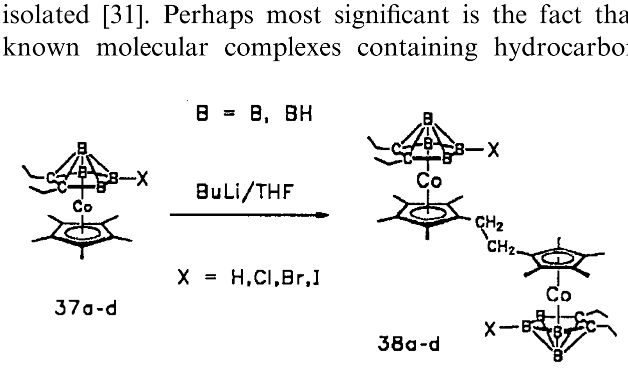
4.5. Cyclooctatriene displacement and synthesis of arene–ferracarborane complexes

The ability of $RR'C_2B_4H_4^{2-}$ ligands to influence the chemistry at metals to which it is bound has been put to good use in the synthesis of arene–iron–carborane sandwich complexes [29], a genre that had earlier proved elusive. As outlined in Scheme 12, cycoocta-triene–ferracarboranes **39** (obtained in the reaction of $C_8H_8^{2-}$ with ferrous ion and $RR'C_2B_4H_4^{2-}$) undergo facile displacement of the η^6-C_8H_{10} ligand by arenes, generating the desired arene sandwiches **40**. In this case it appears that coordination of the electron-rich metal center to the cyclooctatriene is weaker than metal–arene bonding, so that formation of the latter species is thermodynamically favored.

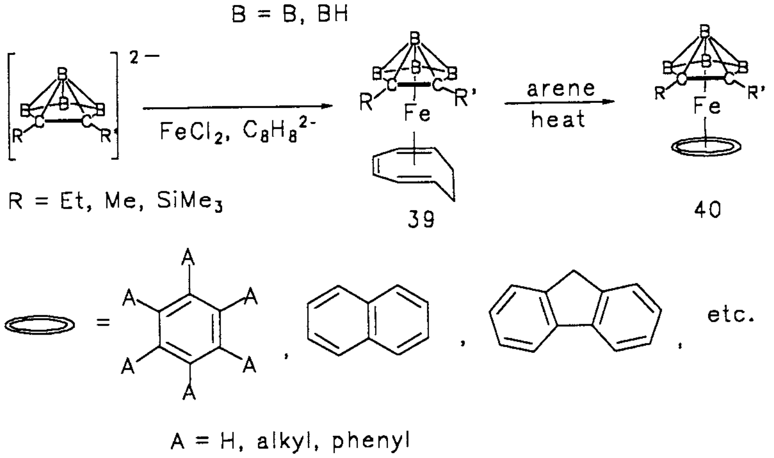
4.6. Metal stacking on C_2B_3 ring ligands

The metal-binding property of small carborane ligands is most powerfully demonstrated in the ability of planar $RR'C_2B_3H_3^{4-}$ ligands to bond tightly to metals on both sides of the ring plane, stabilizing multidecker sandwich complexes so effectively that a wide range of them has been prepared [1a,d,f,22]. The C_2B_3 carborane rings are generated from C_2B_4–metal complexes (not from the free carborane) by base-promoted removal of the apex BH unit to give the corresponding C_2B_3–metal sandwich whose open face, in neutral species, contains two B–H–B bridging protons. One or both of these can be removed to form the mono- or dianionic complex, from which multidecker sandwiches are prepared by metal insertion (Scheme 13).

An appreciation of the stabilizing power of the carborane rings in these complexes—which are typically very robust, air- and thermally stable molecules —can be gained by comparison with the few known hydrocarbon-bridged multidecker species. The only known isolable complex in which a C_5H_5 unit is sandwiched between two metals is the classic Cp_2Ni^+ ion, the first triple-decker [30], which is extremely reactive with air and water; triple-decker sandwiches bridged by Cp* (C_5Me_5) or arene units are somewhat more resistant to degradation, but only a few such species have been isolated [31]. Perhaps most significant is the fact that known molecular complexes containing hydrocarbon



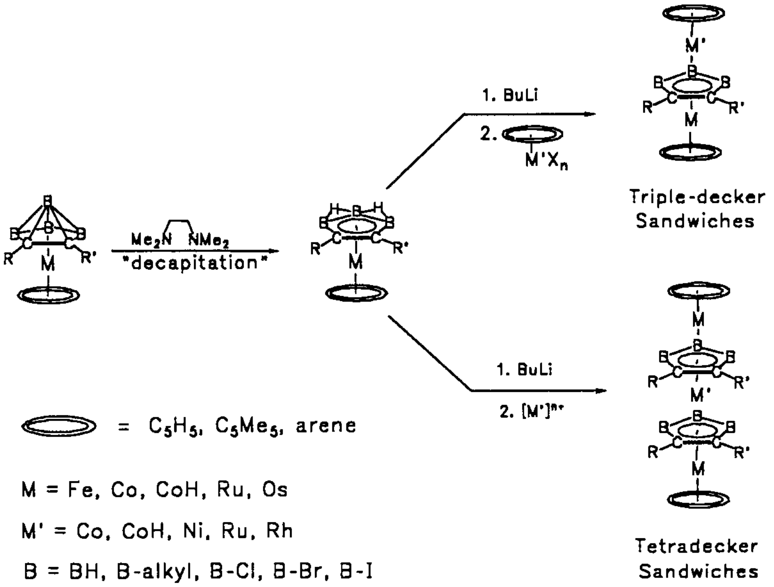
Scheme 11.



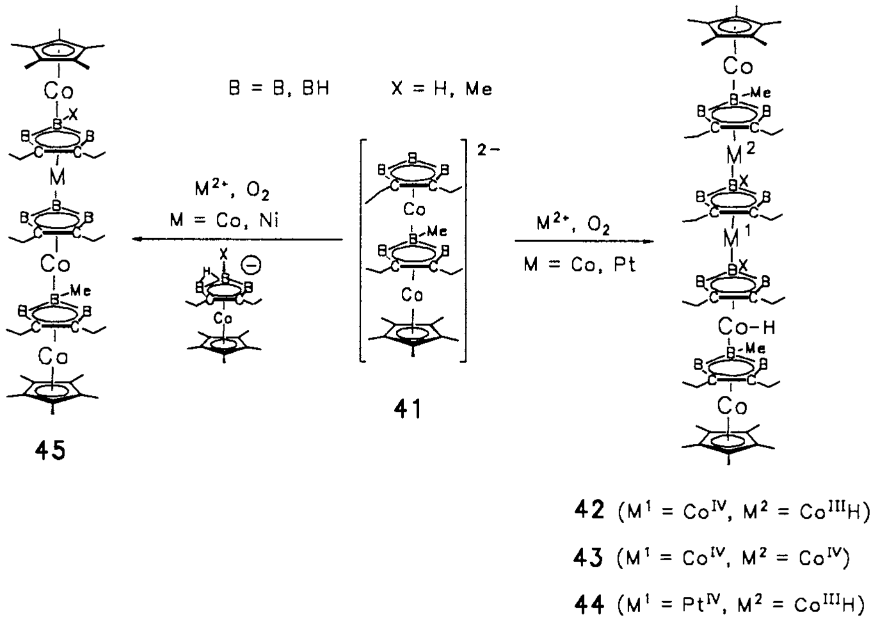
Scheme 12.

rings that are fully sandwiched between two metals (not staggered) are limited to triple-deckers. Indeed, all reported examples of multideckers having four or more decks incorporate either C_2B_3 or C_3B_2 (diborolyl) rings [1a,b,d,32]. The ability of C_2B_3 and C_3B_2 ring ligands to stabilize multidecker sandwich structures appears to be without limit, at least in principle, the main constraint being the need to develop useful synthetic routes to larger (ultimately polymeric) sandwiches. Nickel and rhodium polymers based on diborolyl ligands, which are insoluble and noncrystalline [33], have in fact been prepared by Siebert's group, who have also made soluble molecular complexes having up to six decks [34].

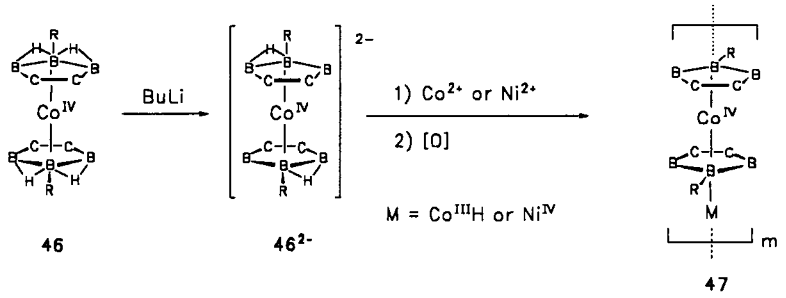
The largest structurally characterized molecular sandwich at this writing is the Co_5 hexadecker **42** containing two Co-bound hydrogens shown in Scheme 14, which depicts the synthesis of carborane-based pentadeckers (**45**) and hexadeckers (**42**–**44**) from the carborane-end-capped triple-decker dianion **41** [35]. Of the three hexadecker complexes isolated in this work, that containing Pt^{IV} (**44**) is diamagnetic while **42** and **43** are paramagnetic Co_5 systems having one and two Co^{IV} centers, respectively. Electrochemical and ESR evidence indicates that the unpaired electrons in **42** and **43** are extensively delocalized over the five metal centers, suggesting that sandwich polymers based on this architecture could function as novel types of one-dimensional electrical conductors. This possibility is currently under investigation in our laboratory, and we have recently prepared building-block double-decker complexes of type **46** which can be deprotonated and combined with metal ions to form polydecker structures such as **47** via self-assembly (Scheme 15) [36]. At this writing, however, well-defined polymeric products have not yet been isolated.



Scheme 13.



Scheme 14.

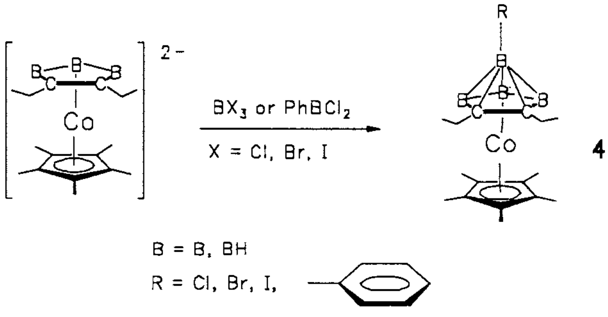


Scheme 15.

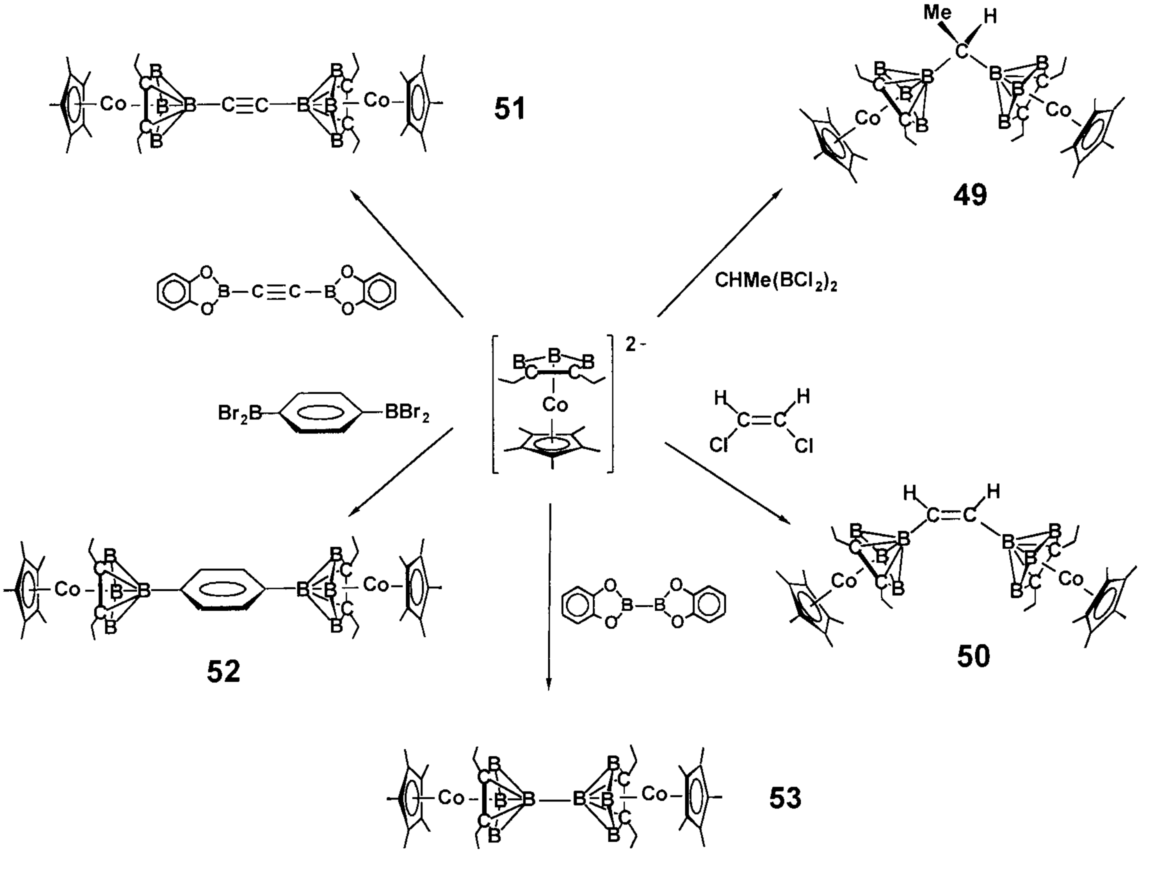
4.7. Boron insertion and linkage via apex boron atoms

An alternative approach to the construction of multicluster/multisandwich extended metal systems, recently developed in our laboratory, employs linkage via the apex (capping) boron atoms on metal-bound C_2B_4 ligands [37]. Substitution of the apex hydrogen had not previously been possible, but this problem has been circumvented by so-called 'recapitation' in which a boron containing the desired substituent is inserted into an open C_2B_3 ring ligand, thereby restoring the C_2B_4 cage as shown in Scheme 16. As in the metal stacking reactions described above, this involves direct action on C_2B_3 ring ligands, which are thus active players in the process. Particularly useful is the synthesis of bimetallic species such as **49**–**53** (Scheme 17) from bis(organoboryl) reagents, all characterized by X-ray crystallography [37]. The variety of complexes that can be generated in this way is underlined by the observation that the linking groups in **49**–**51** have respectively sp^3-, sp^2-, and sp-hybridized carbon atoms while **53** has a direct apex-to-apex boron–boron link. (An isomer of **53** having a B–B connection between the middle equatorial borons has recently been prepared via 'inorganic Wurtz reactions' of Cp*Co(2,3-$Et_2C_2B_4H_3$-5-X) (X = Cl, Br, or I) with sodium metal in THF [27]).

Owing to their capping Cp* ligands, the apex-linked species **49**–**53** are not suited as building-blocks for linear sandwich polymers, but analogous complexes having C_2B_3-containing end rings in place of hydrocar-



Scheme 16.



Scheme 17.

bons would be ideal for such purposes via stacking reactions with metal cations or bifunctional boron-inserting reagents. Compounds of this type having open carborane end ligands have recently become available in our laboratory, and their potential as polymer precursors is under study.

5. Summary

In this article, I have attempted to highlight the similarities and differences between the small carborane ligands and their isoelectronic 6-electron donor η^5-hydrocarbon analogues, with special emphasis on novel reaction modes not seen in metal–Cp or metal–Cp* sandwich chemistry. The examples discussed here illustrate two basic points. First, the carborane ligands are capable of functioning as isoelectronic surrogates for Cp or Cp* (spectators), but because of their electron-donating ability they can stabilize abnormally high formal metal oxidation states and unusual metal–ligand architectures. Second, in many cases the carborane units participate directly in reactions with organic and inorganic substrates, undergoing structural and compositional change in the process. It is in this latter area that the contrast with metallocene and metal–arene chemistry is most dramatically evident.

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